Magnetoelectric properties of multiferroic $FeVO_4$

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Abstract

We report the magnetic, dielectric and ferroelectric properties of polycrystalline iron vanadate($FeVO_4$), which has been recently found to exhibit multiferroicity in low temperature with noncollinear magnetic orderings. The influence of external magnetic field up to 9T on these properties is systematically investigated. Besides the suppression of the original multiferroic ferroelectric transition, the magnetic field also induced a secondary ferroelectric transition at lower temperature. And the corresponding field-dependent magnetization measurement reveals a metamagnetic transition at low temperatures. Our results will help to clarify the detailed magnetic structure and microscopic mechanism of multiferroicity in $FeVO_4$.

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I. INTRODUCTION

Stimulated by the recent discovery of strong coupling of magnetism and ferroelectricity in some frustrated manganites as $TbMnO_3$ and $TbMn_2O_5$ [1, 2], the research on multiferroics has attracted worldwide attention. In these materials, both magnetic order and ferroelectric coexist. Although this kind of coexistence has been discovered decades ago, most known multiferroic materials, e.g. BiFeO3, show weak magnetoelectric coupling because their ferroelectricity and magnetism come from different ions in the unit cell, with partially filled d shells and empty d shells respectively. These two orderings, therefore, tend to be mutually exclusive and interact weakly with each other[3]. On the contrary, the ferroelectricity found in these frustrated manganites is of magnetic origin, i.e., induced by complex spin structure. The spontaneous electric polarization occurs in special magnetically ordered states which break the inversion symmetry, and the electric polarization can even be inverted via changing the magnetic states by external magnetic field. The fascinating phenomena are of great importance both for the fundamental physics and potential technological application [4].

There are several reported types of magnetic orders that can break the space inversion invariance and produce spontaneous electric polarization. For example, the inequivalent nearest-neighbor exchange striction in the commensurate collinear $\uparrow\uparrow\downarrow\downarrow$ spin chains can shift ions away from centrosymmetric positions and induce the polarization along chains. But most of the realistic multiferroic frustrated magnets are of much more complex spin structures, which are usually incommensurate and noncollinear at low temperatures. One of the commonly accepted microscopic mechanism comes down to the inverse Dzyaloshinskii-Moriya(DM) interaction, which was first proposed as an antisymmetric relativistic correction to the superexchange coupling[5]. It can also be expressed in the equivalent spin current model by Katsura, Nagaosa and Balatsky(KNB)[7]. According to their theoretic analysis, the microscopic polarization induced by neighboring spins can be formulated as $\mathbf{P}_{ij} = A\hat{\mathbf{e}}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$, where the coupling constant A is determined by the spin-orbit coupling and exchange interactions in the system. And $\hat{\mathbf{e}}_{ij}$ is the unit vector connecting site i and j. It is also consistent with the corresponding phenomenological symmetry analysis[8], and has worked well in the helimagnetic $TbMnO_3$ and other multiferroics[6]. But the accurate prediction of the magnitude still lacks at present since much more complicated factors in real systems must be considered.

On the other hand, according to the known microscopic mechanism of magnetoelectric coupling, the investigation on the polarization and dielectric properties of multiferroic compounds can also help us explore the complex magnetic structures, which traditionally have been characterized by the much more difficult and expensive experimental techniques such as neutron diffraction [9].

At present, our particular interest is on the recently discovered multiferroicity in iron vanadate($FeVO_4$). The crystal structure and magnetic properties of $FeVO_4$ have been investigated during the early 1970s[10, 11]. $FeVO_4$ have a triclinic crystal structure (Ref:PDF number 71-1592 space group $P1\bar{1}$, a=6.719Å, b=8.060Å, c=9.254Å, α=96.4°,β=106.8°, γ=101.5°), which is shown in Fig. 1. The magnetism of $FeVO_4$ comes from the Fe^{3+} ions at three different sites, which is orbitally quenched and in the high spin $S = 5/2$ state. The Fe^{3+} ions form a peculiar chain-like structures, well separated by non-magnetic VO_4 tetrahedrons. The complex Fe-O-Fe superexchange (SE) and Fe-O-0-Fe super-superexchange(SSE) interactions between Fe^{3+} ions lead to the magnetic frustration in $FeVO_4$, and therefore complex magnetic behavior.

From the recent results of susceptibility and heat capacity measurements[12–16], $FeVO_4$ undergos two successive magnetic transitions at about T_{N1} $\simeq$22K and T_{N2} $\simeq$15K. The preliminary neutron diffraction measurement in zero field revealed a spiral spin structure at lower temperature ($T<T_{N2}$), while a collinear antiferromagnetic(AFM) order in the intermediate state($T_{N2}<T<T_{N1}$)[14]. The two kinds of magnetic structures are both incommensurate but the ferroelectricity is found only concomitant with the non-collinear magnetic order at low temperature. The physical nature of its multiferroicity, however, remains elusive. The detailed magnetic structure and corresponding evolution with external field deserve further in-depth research. Till now, there is only a few reports on the multiferroic $FeVO_4$. Therefore, in this paper, we carried out the systematically magnetic and dielectric measurements on polycrystalline $FeVO_4$ at low temperatures. Out work will help to determine the complex magnetic structures and further unravel the microscopic mechanism of the multiferroicity in $FeVO_4$.

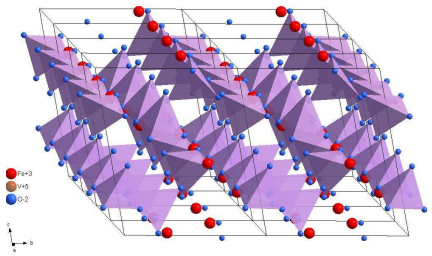

FIG. 1: Schematic crystal structure of $FeVO_4$

II. EXPERIMENTAL

The polycrystalline $FeVO_4$ are prepared by conventional solid-state reaction using high-purity Fe_2O_3 and V_2O_5 as staring materials. The detailed procedures were described elsewhere[10]. It is notable that V_2O_5 is volatile and reacts with alumina crucible at high temperature, which leads to the heavy contamination of the samples. The use of alumina crucibles should therefore be avoided, and instead, a platinum crucible with a cover is recommended in the sinter procedure.

Magnetic properties were measured on a SQUID magnetometer(MPMS-5S, Quantum Design) and a 9T-Physical Properties Measurement System (PPMS) with a magnetization option. To measure dielectric properties of $FeVO_4$, the polycrystalline sample is polished to a thin plate with thickness of about $0.2mm^2$. We use silver epoxy attached to both sides as electrodes to form a parallel plate capacitor whose capacitance is proportional to the dielectric constant(ϵ_r). The samples are glued on the cryogenic stage of our homemade probe, and connected to a high-precision capacitance meter. The main sources of error such as residual impedance in the whole circuit, are carefully considered and compensated. Our measure system has been tested with the standard commercial capacitors(0.5-10pF), which is close to our samples.

The electric polarization (P) is obtained from the integration of the measured pyroelectric current. We first poled the sample during the cooling process with applied electric field of about 400kV/m, then removed the field and shorted the sample at low temperature for at least 30 minutes to discharge the free charge carriers. The pyroelectric current was measured with a warming rate of 3K/min.

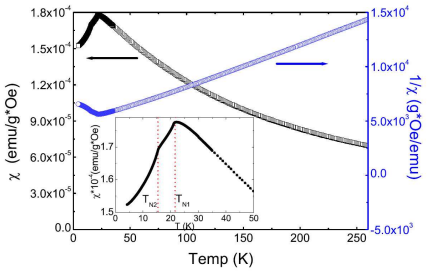

FIG. 2: the temperature-dependent magnetic susceptibility and the corresponding inverse susceptibility of $FeVO_4$ measured in a magnetic field of 1000Oe. The susceptibility at low temperatures is also shown in the inset and the two magnetization anomalies are marked by the red dashed lines.

III. RESULTS AND DISCUSSIONS

Fig. 2 shows the temperature dependence of magnetic susceptibility(χ) and corresponding inverse one(χ^{-1}) measured in the field of H=1000Oe. At high temperature(T>30K), a typical Curie-Weiss paramagnetic behavior is observed, i.e., $\chi = C/(T-\theta)$. The effective magnetic moment(μ_{eff}) in the paramagnetic phase is about $5.96\mu_B$, which is deduced from the fitted Curie constant C. It is very close to $5.916\mu_B$, the expected value for $S = 5/2$ Fe^{3+} ions in a high spin state. The fitted θ=-112K suggests the main antiferromagnetic interaction existing between Fe^{3+} ions.

As temperature decreases, two magnetization anomalies are observed at T_{N1}=21.7K and T_{N2}=15.4K. This is in good agreement with the previous experiments [10, 11, 13, 15], suggesting two different magnetic ordering states at low temperature, $T_{N2}<T<T_{N1}$ and $T<T_{N2}$ respectively. As disclosed in the neutron diffraction measurement by Daoud-Aladine et al [14], the helical magnetic order exists at $T<T_{N2}$ and the collinear AFM spin density wave exists in the intermediate state($T_{N2}<T<T_{N1}$). It is also noted that the corresponding transition temperatures reported by He et al [12], 20K and 13K, are quite lower, possibly due to the Al contamination from the alumina crucibles used in the crystal growth process.

In Fig. 3(a) shows the raw data of the temperature-dependent sample capacitance in zero field, which is proportional to the dielectric constant of $FeVO_4$. The most remarkable feature is the sharp peaks of dielectric anomaly at T_{N2}, which is clearly observed for all our testing frequencies(from 50kHz to 1MHz). Evidently, these dielectric peaks are associated with the emerging of ferroelectric order. Around T_{N1}, there is a slight but not non-negligible discon-

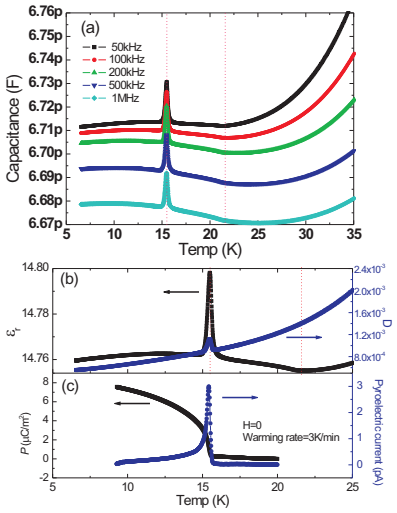

FIG. 3: (a) the temperature dependence of the capacitance of a typical $FeVO_4$ sample measured at different testing frequencies in zero field. (b) the dielectric constant(ϵ_r) and corresponding tan loss(D)measured at freq=100kHz, and (c) pyroelectric current measured at a warming rate 3K/min after cooling the $FeVO_4$ sample with a poling electric field over 400kV/m and succedent discharging at low temperature. The polarization(P) is acquired by integrating pyroelectric current.

tinuity in ϵ_r(T)(see (b) for details). A small excess increase of ϵ_r occurs as T<T_{N1} and the frequency independence indicated the intrinsic transition associated with the corresponding appearance of new magnetic orderings. The slight anomaly at T_{N1} is also consistent the recent observation on $FeVO_4$ thin films by Dixit et al[16]. For convenience, we adopt only the data measured at 100kHz in our following discussions.

Further evidence of the ferroelectric transition at T_{N2} is shown in Fig. 3(b). There is a clear peak in the dielectric loss of $FeVO_4$ at T_{N2}, coinciding with the peak in ϵ_r(T). It is a typical feature of proper ferroelectric transition. But no peak or anomaly of dielectric loss appears around T_{N1}. This confirms that the ferroelectricity is only concomitant with the collinear magnetic state in low temperature, which is consistent with the inverse DM mechanism. We also measured the corresponding electric polarization by integrating the pyroelectric current. The spontaneous polarization P is about 7.3μC/m^2 as T=10K, in agreement with previous measurements[13, 15, 16]. The P can be reversed by an opposite poling electric fields (not shown here), confirming the ferroelectric nature in the T<T_{N1}.

To further disclosed the magnetoelectric coupling and the possible effect of external mag-

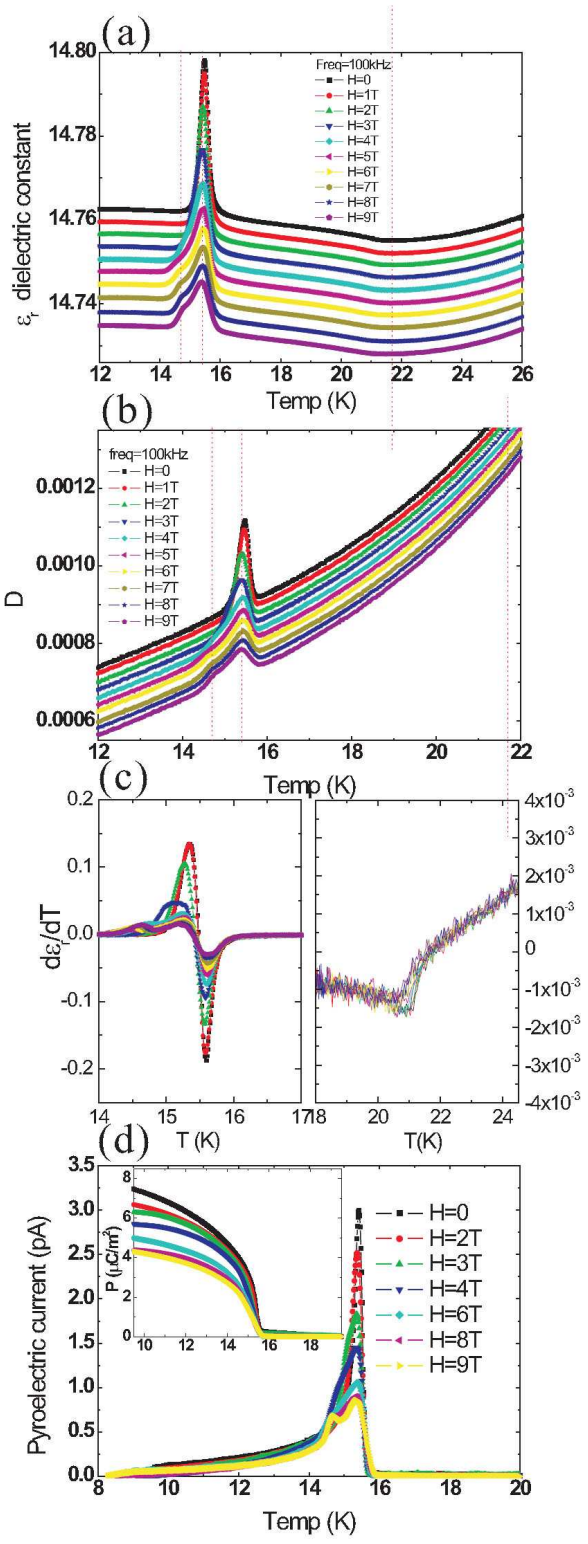

FIG. 4: (a) and (b) are the temperature dependence of dielectric constants(ϵ_r) and corresponding dielectric loss(D) measured in different field(H=0-9T). the data are shifted vertically for clarification except the H=0 case. (c) is the temperature derivative of dielectric constants, dϵ_r/dT, around the two successive transitions respectively.(d) the pyroelectric currents measured at a fixed warming rate of 3K/min in different H from 0 to 9T. The corresponding electric polarization (P) is shown in the inset of (d).

netic field on the complex spin structures, we measure the ϵ_r(T) in different magnetic fields. In our experiments, there is no discernable difference between the two H⊥E and H∥E measuring configurations, since the intrinsic anisotropy in $FeVO_4$ can be cancelled out in our polycrystalline bulk samples.

As shown in Fig. 3(a), around the first magnetic transition at T_{N1}, the slight increase in ϵ_r(T) remain almost unchanged by external field up to 9T. For clarification, the corresponding temperature derivative of ϵ_r(T) is plotted in Fig. 3(c). The evident variance in $d\epsilon_r(T)/dT$ curves exists around T_{N1} and is almost unchanged in different fields.

The most striking feature induced by magnetic field occurs around the second magnetic transition at T_{N2}. The sharp peak of dielectric anomalies in zero field is gradually suppressed by increasing external magnetic fields. However, the shift of the corresponding transition temperature T_{N2}(∼15.4K), which is defined by the maximum of ϵ_r(T) peak, is too slight and can be negligible even in the highest field H=9T.

Another significant characteristic is the emergence of a new hump of dielectric anomaly around the T_{N3}≃14.7K (slightly lower than T_{N2}), when the applied field exceeds 3T. As H increases further, the secondary dielectric hump around T_{N3} grows gradually along with the further suppression of the magnitude of dielectric peak at T_{N2}. The shift of T_{N3} is also negligible in different fields. To demonstrate the fine variance in the structure of ϵ_r(T) induced by H, the temperature derivative of ϵ_r(T) around T_{N2} and T_{N3} is also plotted in the left part of Fig.3(c).

It is apparent that there exists a magnetic field-induced new transition at T_{N3}. To determine the nature of this transition, we also measured the corresponding dielectric loss shown in Fig.3(b). The evolution of D(T) with external magnetic field is quite similar with the ϵ_r(T) except absence of anomaly around T_{N1}. The hump in D(T) at T_{N3} suggests a new proper ferroelectric transition induced by external magnetic field.

The field-induced ferroelectricity around T_{N3}, is also verified in our pyroelectric measurements. The pyroelectric current measured in different fields at a fixed warming rate(shown in Fig.3(d)) is proportional to the temperature derivative of electric polarization (dP/dT) and better reveals the field-induced fine change than the P(T) curves. The pyroelectric current peak in zero field, which marks the emerging of the spontaneous polarization arising at T_{N2}, is suppressed greatly by external magnetic field. However this suppression by magnetic fields seems to saturate as H≥8T. When H>3T, the secondary peak of the pyroelectric current

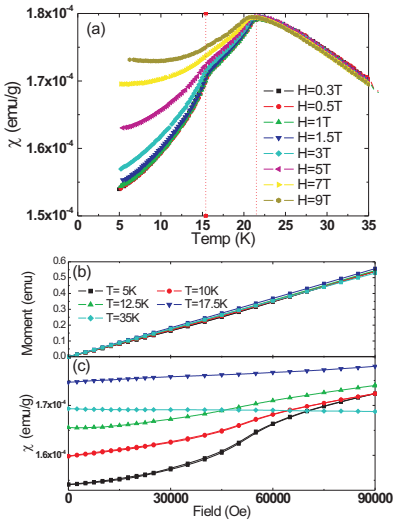

FIG. 5: (a) the temperature-dependent magnetic susceptibility of $FeVO_4$ measured in different fields(0.3-9T) on a 9T PPMS. (b) The magnetic field dependence of magnetization of $FeVO_4$ measured at several temperatures(T=5K, 10K, 12.5K, 17.5K, 35K) with field ranged from 0-9T. Corresponding magnetic susceptibilities are plotted in (c).

emerges and develops with growing H. The new field-induced ferroelectricity below T_{N3} is confirmed. The corresponding polarization acquired by integrating pyroelectric currents is shown in the inset. At low temperature, the total P includes these different contributions which are hard to be separated. P decreases with growing H and seems saturated when H$\geq$8T.

To our knowledge, it is the first time that this field-induced new multiferroic transition is observed in the $FeVO_4$ system. This is partially due to our highly accurate and careful measurements.

We also carried out the magnetization measurements in different fields(H=0.1-9 T)and the results are shown in Fig. 5(a). The first magnetization anomaly at T_{N1} is evident up to 9T with negligible temperature shift, consistent with the corresponding dielectric measurements(see Fig. 3(a)and (c)). The second magnetization anomaly at T_{N2} can be clearly discerned at low fields(<5T), but gradually fades away with increasing up-turn background as H grows, and finally become almost indistinguishable in H=9T.

To further explore the change of the low-temperature magnetic states, we measured a field-dependent magnetization(M-H), which is shown in Fig.5(b). The deviation from

the linearity is quite small in M-H curves, but can be manifested in the corresponding susceptibility curves (χ(H)) , as shown in Fig.5(c).

At high temperature such as T=35K>T_{N1}, the quite linearity of the M-H curve and nearly constant χ(H) up to 9T is a typical behavior for the paramagnetic state. As in the intermediate state between T_{N1} and T_{N2}(T=17.5K), the χ(H) deviates slightly from the constant and grows slightly with increasing H. The increase in χ come possibly from the partial suppression of the incommensurate collinear antiferromagnetic ordering by external magnetic field.

When cooled further down to T= 10 and 5 K (both well below T_{N2}), the noncollinear incommensurate magnetic ordering exists in $FeVO_4$, which is disclosed in recent neutron diffraction experiment[14]. The nonlinearity in M-H curves becomes more pronounced. Especially, a broad kinking appears in χ(H), centering around 4.5T. At high fields, the χ(H) at 5K and 10K seems to merge together, suggesting a new common stable magnetic ground state in strong field. Our data at T<T_{N2} indicates a field-induced metamagnetic transition, although its origin is still unclear. These features are also consistent with the above evolution of the ferroelectric properties and especially the new field-induced ferroelectric transition at T_{N3}. The new magnetic phase must be also noncollinear in nature according to the inverse DM mechanism on multiferroicity.

Since the multiferroicity is usually highly anisotropic and only bulk average properties can be acquired on our polycrystalline samples, the growth of large single crystals is necessary to explore the anisotropic intrinsic dielectric response and electric polarization to unravel the complex magnetic orderings via magnetoelectric coupling in multiferroic $FeVO_4$ [9]. The effect of the partial substitution of Fe^{3+} by other ions is also our work under way. Our speculation about the new field-induced multiferroic state requires the further confirmation from future neutron diffraction experiments in strong magnetic fields.

IV. SUMMARY

In summary, we have investigated the dielectric and ferroelectric properties of polycrystalline $FeVO_4$ in external magnetic field with high accuracy together with corresponding magnetization measurements. The two successive magnetic transitions occur at low temperatures(T_{N1} and T_{N2} respectively). The multiferroicity emerging below T_{N2} is con-

firmed and found to be strongly suppressed by external magnetic field. At the same time, a secondary field-induced ferroelectric transition is found in strong field at $T_{N3}(<T_{N2})$, consistent with the metamagnetic transition observed in field-dependent magnetization measurements. Further neutron diffraction measurements on $FeVO_4$ in strong fields is expected to confirm this issue.

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